

PHOSPHORESCENT TRINUCLEAR GOLD(I) PYRAZOLATE COMPLEX  
BEARING PHOTOCHROMIC AZOBENZENE SIDE-CHAINS

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## ABSTRACT

Photochromic soft materials have received particular attention for inducing excellent properties in many fields such as displays, sensor, energy, catalysts, molecular electronics, and memory. In particular, organometallic compounds such as Group 11 azolate complexes with luminescent properties reveal promising characteristics from supramolecular self-assembly of columnar nanostructures upon ultraviolet and visible light treatments. Although self-assembled nanostructures with azobenzene moieties have been used to study photochromic *cis-trans* isomerization towards light irradiation, there is no example for the utilization at the side-chains of the metal complexes. Herein, this study reports the first successful synthesis of phosphorescent trinuclear gold(I) pyrazolate complex bearing hydrophobic azobenzene side-chains. The gold complex (**7**) was synthesized via seven stepwise reactions and named as tris[(*E*)-3,5-dimethyl-4-(4-((4-propoxyphenyl)diazenyl)benzyl)-1*H*-pyrazolato-*N,N'*]trigold(I) (**7**, 28%). Compound **7** showed *cis-trans* isomerization upon UV and visible light irradiation at 365 nm and 535 nm, respectively. Interestingly, metal-metal interaction was not affected by the *cis-trans* photoisomerization. Compound **7** showed emission of a combination of 423, 472 and 537 nm with excitation wavelength of 271 nm, large stoke shift of 266 nm suggested the emission to be phosphorescence. Compound **7** was able to show white phosphorescence in dried solid state, which was resulted from the region of blue, green and red emission. Compound **7** was non-emissive in CHCl<sub>3</sub>, but able to regain emission upon addition of water which decreased the solubility of compound **7** in CHCl<sub>3</sub>. Successful formation of metal-metal interaction directly related to the phosphorescence of compound **7**, which can be utilized as aggregation-induced emissive (AIE) material with photochromic properties.

## ABSTRAK

Bahan lembut fotokromik telah menerima perhatian khusus untuk mengaruh sifat yang sangat baik dalam pelbagai bidang contohnya paparan, pengesan, tenaga, mangkin, elektronik molekul, dan memori. Khususnya, sebatian-sebatian organologam contohnya kompleks azolat kumpulan 11 dengan sifat pendarcahaya, mendedahkan ciri-ciri yang menjanjikan disebabkan oleh penswahimpunan supramolekul struktur nano berturus apabila dirawat dengan cahaya ultra ungu dan cahaya nampak. Walau struktur nano terswahimpun dengan moeiti azobenzena telah digunakan untuk mengkaji pengisomeran *cis-trans* fotokromik ke arah penyinaran cahaya, tiada contoh penggunaannya pada rantai sisi kompleks logam. Kajian ini melaporkan sintesis pertama yang berjaya bagi kompleks pirazolat aurum(I) trinukleus pendarfosfor yang mempunyai rantai sisi azobenzena fotokromik. Kompleks aurum (**7**) telah disintesis melalui tujuh tindak balas peringkat demi peringkat dan dinamakan sebagai tris[(*E*)-3,5-dimetil-4-(4-((4-propoksifenil)diazenil)benzil)-1*H*-pirazolato-*N,N'*]triAurum(I) (**7**, 28%). Sebatian **7** menunjukkan pengisomeran *cis-trans* apabila disinari dengan cahaya UV dan cahaya nampak masing-masing pada 365 nm dan 535 nm. Apa yang menarik, interaksi logam-logam tidak terjejas oleh proses pemfotoisomeran *cis-trans*. Sebatian **7** menunjukkan pancaran pada gabungan 423, 472 and 537 nm dengan panjang gelombang pengujaan 271 nm, anjakan Stoke yang besar sebanyak 266 nm mencadangkan pancaran tersebut adalah pendarfosfor. Sebatian **7** mampu mempamerkan pendarfosfor putih dalam keadaan pepejal terhasil daripada pancaran dalam kawasan biru, hijau dan merah. Sebatian **7** tidak menghasilkan pancaran di dalam CHCl<sub>3</sub>, tetapi mampu menghasilkan pancaran selepas ditambah air yang menurunkan keterlarutan sebatian **7** di dalam CHCl<sub>3</sub>. Kejayaan pembentukan interaksi logam-logam adalah berkaitan secara langsung dengan pendarfosfor sebatian **7**, yang boleh digunakan sebagai bahan pancaran pengagregatan teraruh (AIE) yang bersifat fotokromik.

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## LIST OF ABBREVIATIONS

BTA-3AZO	- Benzene-1,3,5-tricarboxamide containing azobenzene
LCE	- Liquid crystal elastomer
Compound 1	- ( <i>E</i> )-ethyl 4-((4-hydroxyphenyl)diazenyl) benzoate
Compound 2	- ( <i>E</i> )-ethyl 4-((4-propoxyphenyl)diazenyl) benzoate
Compound 3	- ( <i>E</i> )-(4-((4-propoxyphenyl)diazenyl) phenyl)methanol
Compound 4	- ( <i>E</i> )-1-(4-(bromomethyl)phenyl)-2-(4-propoxyphenyl)diazene
Compound 5	- ( <i>E</i> )-3-(4-((4-propoxyphenyl)diazenyl)benzyl) pentane-2,4-dione
Compound 6	- ( <i>E</i> )-3,5-dimethyl-4-(4-((4-propoxyphenyl)diazenyl)benzyl)-1H-pyrazole
Compound 7	- tris[ <i>E</i> ]-3,5-dimethyl-4-(4-((4-propoxyphenyl)diazenyl)benzyl)-1H-pyrazolato- <i>N,N'</i> ]trigold(I)
C <sub>3</sub> H <sub>7</sub> Br	- 1-bromopropane
LiAlH <sub>4</sub>	- Lithium aluminium hydride
THF	- Tetrahydrofuran
CBr <sub>4</sub>	- Tetrabromomethane
PPh <sub>3</sub>	- Triphenylphosphine
KOH	- Potassium hydroxide
<sup>1</sup> H-NMR	- Proton-1 Nuclear Magnetic Resonance
<sup>13</sup> C-NMR	- Carbon-13 Nuclear Magnetic Resonance
FTIR	- Fourier-Transform Infrared Spectrometer
MALDI-TOF MS	- Matrix-Assisted Laser Desorption/Ionization-Time of Flight Mass Spectrometer
UV-Vis	- Ultraviolet-Visible light
LED	- Light-emitting diode
AIE	- Aggregation-induced emission
BTA	- Benzotriazole

NaCl	-	Sodium chloride
PVA	-	Poly(vinyl alcohol)
LDLCF	-	Light driven liquid-crystal film
<sup>n</sup> Bu <sub>4</sub> NCl	-	Tetra-n-butylammonium chloride
DMSO	-	Dimethyl sulfoxide
PSS	-	Photostationary state
SEM	-	Scanning Electron Microscope
AgOTf	-	Silver trifluoromethanesulfonate
KBr	-	Potassium bromide
TLC	-	Thin-layer chromatography
HCl	-	Hydrochloric acid
NaNO <sub>2</sub>	-	Sodium nitrite
MeOH	-	Methanol
NaOH	-	Sodium hydroxide
CH <sub>2</sub> Cl <sub>2</sub>	-	Dichloromethane
K <sub>2</sub> CO <sub>3</sub>	-	Potassium carbonate
DMF	-	<i>N, N</i> -dimethylformamide
Na <sub>2</sub> SO <sub>4</sub>	-	Sodium sulfate
EtOAc	-	Ethyl acetate
NaHCO <sub>3</sub>	-	Sodium hydrogen carbonate
MgSO <sub>4</sub>	-	Magnesium sulfate
N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O	-	Hydrazine monohydrate
CaCl <sub>2</sub>	-	Calcium chloride
[Au(S(CH <sub>3</sub> ) <sub>2</sub> )]Cl	-	Chloro(dimethyl sulfide)gold(I)
1		
HPLC	-	High-Performance Liquid Chromatography
CDCl <sub>3</sub>	-	Deuterated chloroform
3D		Three-dimensional



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# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

Photochromic materials are known for their flexibility in structural arrangement upon the light irradiation of different but specific wavelength. Energy absorbed by the chromophore is stabilized and this process requires the adjustment of geometrical structure. For example, azobenzene changes from *trans*-form to *cis*-form after being irradiated by ultraviolet light at 300-400 nm and reversed back from *cis*-form to *trans*-form after being irradiated by visible light at 435-500 nm [1]. Furthermore, the fact that light as a free, clean, renewable and sustainable energy source has made photochromic materials unavoidable building part in developing smart materials.

Azobenzene has been used to fabricate various smart materials in different fields over the past decades. In surface and coating, the reworkable adhesive was fabricated using multiazobenzene sugar-alcohol derivatives [2]. Besides, mesoporous nanocontainer with azobenzene switches was fabricated for the purpose of continuous self-healing anticorrosion coating [3]. Furthermore, light-responsive bio-materials were also pursued mechanical purpose such as actuation properties. For example, a benzene-1,3,5-tricarboxamide containing azobenzene (BTA-3AZO) was synthesized and tested for the application of rewritable films and remote-controlled three-dimensional (3D) actuation [4]. A light-responsive film was also fabricated using a thin film coated with a mixture of liquid crystal elastomer (LCE) and azobenzene as the photochromic motif. The photochromic LCE film was used to mimic the gripping action as the Venus flytrap [5] and the actuating mechanics were able to be applied as smart microrobots. Besides, these azobenzene-containing LCE was also fabricated into strip form and into belt form to mimic caterpillar locomotion [6] and rolling motion [7], respectively. In addition, a light-driven swimmer with

griper was also fabricated successfully by utilizing photoisomerization of azobenzene in the material used [8]. With many successful examples of light-responsive actuators, azobenzene-containing materials were also found useful in fabricating artificial cilia [9] that have great potential in producing flow, enabling 'lab-on-a-chip' and even used to create artificial organs such as esophagus and intestine. Therefore, photochromic materials have shown great potential as the smart material that can be controlled easily and remotely by using light as the sustainable and renewable energy source.

Great attention has been given by the researchers on this photochromic material. The azobenzene units were incorporated as photochromic motif into the metal complexes, ranging from iron, zinc, nickel, copper, palladium, platinum and gold, thus producing photochromic metal complexes. The first attempt was carried out back to 1969 by Murray [10] to synthesize azobenzene-conjugated platinum(II) terpyridine complexes. As in 2007, gold(I) alkynyl phosphine complex containing azobenzene was documented [11]. In 2010, nickel(II) and palladium(II) complexes using azobenzene-containing ligands were synthesized [12]. While in 2011, Yeap and colleagues [13] synthesized copper(II) and nickel(II) complexes with ligands derived from azobenzene-cored Schiff base. In 2012, palladium(II) complexes with azobenzene-containing ligands were synthesized [14]. In 2013, Savel and colleagues [15] synthesized platinum(II) complex with ethylene-linked azobenzene ligands. Besides, palladium(II) complexes with azobenzene-containing ligands were reported [16]. On the other hand, metal complexes from zinc(II), copper(II), iron(II) and other transition metals with azobenzene-functionalized imine-based ligands were synthesized [17], whereas Deibel and colleagues [18] came out with platinum(II) complexes from azobenzene and zwitterionic quinonoid ligands. Most recently in 2019, rhenium(I) complexes were prepared using azobenzene iminopyridine ligands[19].

Notably, the study on gold complex incorporated with azobenzene is rarely seen in past decades. This is especially true for gold species which has an oxidation number of +1 and high stability. Gold is special for its aurophilic interaction via configuration complexation. There is a scarce amount of studies carried out on gold(I) metal complex incorporated with photochromic motif such as azobenzene. Alkynyl

phosphine ligands are one of the reported examples. However, there is another emerging family for the gold(I) complex with pyrazole ligands. Back to 1998, Kim and colleagues [20] reported on hexagonal columnar gold(I) pyrazolate complex bearing three alkyl side chains. In 2001, Aida and colleagues [21] synthesized trinuclear gold(I) pyrazolate complex with dendritic side chains to form phosphorescent fibers. Besides, in 2004, Kishimura and colleagues [22] reported a trinuclear gold(I) pyrazolate bearing long alkyl side chains to form metallogel in hexane. The metallogel was able to be altered upon heating-cooling treatment and doping-dedoping of silver ions on its phosphorescent color-tuning in the range of red-green-blue (RGB).

However, the potential of gold(I) pyrazolate complexes incorporated with photochromic motif such as azobenzene has yet to be explored. This study presents the synthesis of novel gold(I) pyrazolate complex incorporated with azobenzene and investigation of the photophysical properties of the complex.

## **1.2 Statements of Problem**

As the member in the family of gold complexes that used pyrazole derivatives as ligands, studies on gold(I) pyrazolate complexes have always been inconsistent throughout the century. Recently, huge numbers of photochromic metal complexes emerged, however gold(I) pyrazolate complex for its photochromic properties is still under studied. This study synthesized the novel gold(I) pyrazolate complex with photochromic properties.

Besides, the information on the relation between photochromic switching of the azobenzene side-chains and the phosphorescence from metal-metal interactions of gold(I) pyrazolate complex is lacking. Together with the continuous interest on exploring gold(I) pyrazolate complex, this study was carried out to investigate on the effect of photochromic azobenzene side-chains onto the physical and chemical properties for the gold(I) pyrazolate complex.

### 1.3 Objectives of the Study

The objectives of this study were:

- i) To synthesize pyrazole ligand incorporated with azobenzene, (*E*)-3,5-dimethyl-4-(4-((4-propoxyphenyl)diazenyl)benzyl)-1H-pyrazole (**6**) via six consecutive steps.
- ii) To synthesize the photochromic gold(I) pyrazolate complex, tris[(*E*)-3,5-dimethyl-4-(4-((4-propoxyphenyl)diazenyl)benzyl)-1H-pyrazolato-*o*-*N,N'*]-tri-gold(I) (**7**) via the Schlenk technique using compound **6**.
- iii) To study the photophysical and phosphorescent properties of complex (**7**).

### 1.4 Scope of the Study

In the preparation of azobenzene, *p*-aminoethyl benzoate and phenol were used in the coupling reaction to synthesize (*E*)-ethyl 4-((4-hydroxyphenyl)diazenyl) benzoate (**1**). For step two Williamson ether synthesis, compound **1** and 1-bromopropane (C<sub>3</sub>H<sub>7</sub>Br) were used to synthesize (*E*)-ethyl 4-((4-propoxy phenyl)diazenyl) benzoate (**2**). For step three reduction, compound **2** was stirred with lithium aluminium hydride (LiAlH<sub>4</sub>) and dried tetrahydrofuran (THF) to synthesize (*E*)-(4-((4-propoxyphenyl)diazenyl) phenyl)methanol (**3**). For step four Appel bromination, compound **3** and tetrabromomethane (CBr<sub>4</sub>) were used in the presence of triphenylphosphine (PPh<sub>3</sub>) to synthesize (*E*)-1-(4-(bromomethyl)phenyl)-2-(4-propoxyphenyl)diazene (**4**). For step five diketo-alkylation, compound **4** and acetylacetone were stirred under reflux to synthesize (*E*)-3-(4-((4-propoxy phenyl)diazenyl)benzyl) pentane-2,4-dione (**5**). For step six Knorr pyrazole synthesis, compound **5** and hydrazine were used to synthesize (*E*)-3,5-dimethyl-4-(4-((4-propoxyphenyl)diazenyl)benzyl)-1H-pyrazole (**6**). In the last step, compound **6** and

chloro(dimethyl sulfide)gold(I) salt in the presence of potassium hydroxide (KOH) using Schlenk technique to synthesize tris[(*E*)-3,5-dimethyl-4-(4-((4-propoxy phenyl)diazenyl)benzyl)-1*H*-pyrazolato-*N,N'*]trigold(I) (**7**). There were various instruments used in order to characterize the synthesized compounds. Throughout the synthetic route to synthesize compound **6**, the Proton-1 Nuclear Magnetic Resonance (<sup>1</sup>H-NMR), Carbon-13 Nuclear Magnetic Resonance (<sup>13</sup>C-NMR), and Fourier-Transform Infrared Spectrometer (FTIR) were used for the characterization. As for the synthesis of compound **7**, Matrix-Assisted Laser Desorption/Ionization Mass Spectrometer (MALDI-TOF MS) and FTIR were used, chemical resources for re-synthesis and instrumentation usage. As for the analysis of photophysical properties of **7**, UV-Vis spectrophotometer used not only to measure the presence of n- $\pi^*$  and  $\pi$ - $\pi^*$  transition which accordance to the presence of azobenzene moiety in compound **7**. This also allowed the real-time monitoring on the photoisomerization occurred in compound **7** by using 365 nm hand-held UV lamp and 535 nm visible-light LED torch as the light sources. Besides, the maxima absorption was used in spectrofluorometer measurement as excitation wavelength in order to excite compound **7**. Both the recorded excitation and emission wavelengths were interpreted and analyzed as the luminescent profile of compound **7**. Lastly, all photographic images were taken using SM-G950FD.

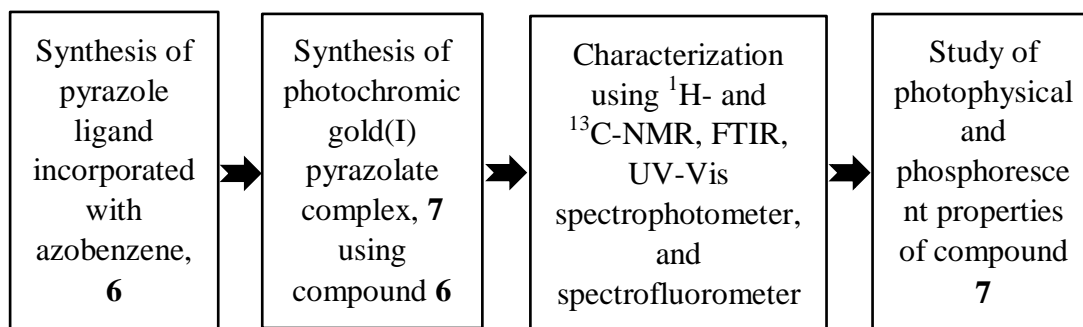
## 1.5 Significance of the Study

In this study, the novel pyrazole ligand using azobenzene moiety, compound **6** was successfully synthesized and further synthesis was carried out to obtain the resulting metal complex, compound **7**. Compound **7** illustrated very interesting behavioral changes upon light irradiation using a hand-held UV lamp at a wavelength of 365 nm and visible light LED torch at a wavelength of 535 nm. At the same time, the solvation test carried out have showed that compound **7** able to exhibit phosphorescent in dried solid state as compared to solvated liquid state. The aggregation behavior was believed to have affected the formation of aurophilic interaction and thus, led to the alteration of phosphorescence for compound **7**. This study served as the herald for other future studies and discoveries such as using

different photochromic groups or by other modifications. The current research findings would contribute to the development of smart materials which illustrate aggregation-induced emission (AIE).

## 1.6 Flowchart of the Study

Flowchart of the study is shown in **Figure 1.1**. The figure illustrates the stagewise studies carried out, starting from synthesis of the pyrazole ligand (**6**), followed by the synthesis of the gold(I) pyrazolate complex (**7**), characterization using spectroscopic techniques such as  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, FTIR, UV-Vis spectrophotometer, and spectrofluorometer, as well as the study of photophysical and phosphorescent properties for the compound **7**.



**Figure 1.1** Flowchart of the study.

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